

## **Synthesis, Characterization and Thermal, Electrical study of CdS-Polyaniline Nanocomposite via Oxidation Polymerization**

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### **ABSTRACT**

Nanocomposites of conducting polyaniline with CdS nanoparticles have been synthesized via chemical Oxidation technique. The effect of CdS-nanoparticles on the electrical conductivity and thermal stability of polyaniline was discussed. The as prepared products were characterized by FT-IR, XRD and Transmission electron Microscopy and TGA thermogram. FTIR absorption band at 3600 - 3500  $\text{cm}^{-1}$  confirmed the highly attached polyaniline with CdS nanoparticles. The XRD study revealed the increased in crystalline nature of nanocomposite. TEM showed the CdS particles are in nanorange with the average diameter of 21 nm which was evenly distributed in polymer matrix. Thermo gravimetric analysis clearly indicated the increased in thermal stability of nanocomposite than the pure PANI. The uniform intercalation of CdS nanoparticles results in a co-operative phenomenon between the polyaniline and the nanoparticles, as a consequence, the CdS nanoparticles increased the electrical conductivity of polyaniline nanocomposite to  $1.79 \times 10^{-3}$  S/cm compared to the pure polyaniline ( $10^{-10}$  S/cm) and Silicon ( $10^{-4}$  S/cm) semiconductors. Its electrical conductivity was found to be analogous with existing semiconducting metals. The fact is supported by the ample of experimental results and characterization evidences.

**Keywords:** Polyaniline, electrical conductivity, thermal stability, cds nanoparticle.

## 1. INTRODUCTION

Polymeric nanocomposites consisting of organic polymer and inorganic nanoparticles in a nanoscale regime represent a novel class of materials that have motivated considerable interest in recent years. These composites exhibit new advantageous properties and can be very different from those of their individual counterparts. It is therefore expected that this type of materials will play increasingly important roles in research and in numerous applications. They frequently have special properties and are significant for many technological applications, ranging from microelectronics to catalysis, optoelectronic devices, and synthesis of lubricant and preparation of electrolytes for rechargeable batteries<sup>1-4</sup>. Polyaniline (PANI) is one of the most interesting conducting polymers due to its low cost, good processability, environmental stability, unique active conduction mechanism<sup>5</sup> and reversible control of conductivity both by charge-transfer doping and protonation<sup>6</sup>. Inorganic semiconductors CdS, ZnS & PbS nanoparticles are the most promising materials used in various applications like sensors, optoelectronic devices and in solar cells. Studies on PANI-CdS nanocomposites have been reported by many researchers<sup>7-10</sup> and focused on electrical conductivity. This paper presents the d.c. electrical conductivity & thermal stability of PANI-CdS nanocomposites in terms of TGA (Thermo-Gravimetric Analysis).

## 2. MATERIALS AND METHODS

All chemicals used in this investigation were of analytical reagent grade and used as received.

Only aniline was distilled prior to use.

### 2.1. Synthesis of Polyaniline via chemical oxidative polymerization

Polymerization was carried out by the chemical oxidation of aniline in the presence of H<sub>2</sub>SO<sub>4</sub> and APS (Ammonium per-sulphate) in 100ml distilled water both played the role as dopant and oxidant respectively. (0.4 mol) APS was dissolved in 100ml distilled water in a four-neck round bottom reaction flask and 0.4mol H<sub>2</sub>SO<sub>4</sub> is also added under mechanical stirring for 2 hours. Aniline (0.4 mol) was stirred with 0.4mol of H<sub>2</sub>SO<sub>4</sub> in 100ml distilled water. The solution of APS in H<sub>2</sub>SO<sub>4</sub> was then added drop-wise in the solution of aniline with vigorous stirring on a magnetic stirrer for 3 hours to initiate the aniline polymerization. The reaction was later carried out at room temperature for 6-7 hours with stirring. A dark green colored PANi suspension was obtained with precipitation. The synthesized PANi was obtained as finely dispersed particles, which were recovered from the polymerization mixture by centrifugation and washed with deionized water repeatedly until the washing liquid was completely colorless. Finally, the mixture was filtered using filtered assembly. After keeping overnight, the dark gray color precipitate was obtained. A precipitate of polyaniline was dried under at 60 – 80°C for more than 8 hours.

## 2.2. Synthesis of PAni-Cds Nanocomposites:

The synthesis steps of PAni/Cds nanocomposite are similar to the synthesis method of PAni. Different amount of Cds were dispersed into the APS solution and stirred for 1 hour prior to the addition of aniline. Aniline (0.4 mol) stirred with 0.4mol H<sub>2</sub>SO<sub>4</sub> in 100 ml of distilled water were added drop-wised using burette into the APS-Cds solution and stirred vigorously to form homogeneous dispersion. For convenience, PAni Composites were prepared with different weight percentages of Cds. Same synthesis conditions were maintained for all composites as that of pure PAni.

### Characterizations

X-RD spectra of all samples were taken on Philips PW -3071, Automatic X-ray diffractometer. Using Cu-K $\alpha$  radiation of wavelength 1.544 Å, continuous scan of 2° / min., with an accuracy of 0.01 at 45 KV and 40 mA. Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 100) of PAni: Cds nanocomposite was studied in the frequency range of 400–4000 cm<sup>-1</sup>. TGA

thermograms of all samples were recorded on Perkin- Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10°C/ min. TGA profile were taken over the temperature range of 30-800°C. The electrical conductivity measurement were made using four probe techniques.

## 3. RESULTS AND DISCUSSION

### 3.1. XRD Study

Fig.1. shows the XRD pattern of pure PAni in emeraldine base form, PAni/Cds Nanocomposite & cadmium sulphide powder. The XRD pattern of PAni shows the two broad peaks at  $2\theta = 20^\circ$  and  $25^\circ$  with (111) & (110) plane and has an amorphous nature<sup>11</sup>. The degree of crystallinity increased in PAni/Cds nanocomposite than pure PAni and Cds, clearly indicated the homogeneous distribution of nanoparticles in the polymer matrix. The crystalline size of the crystalline particle can be determined using Debye Scherer formula [ — ] and it is found that the grain size of PAni/Cds nanocomposite is (27.73nm).

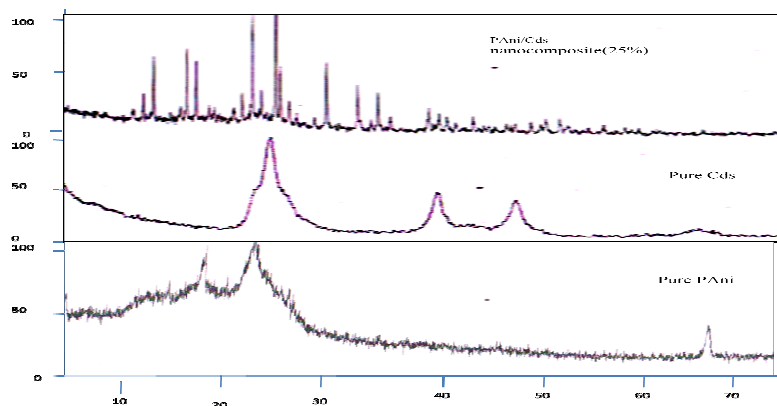


Fig.1. XRD pattern of Pure PAni, pure Cds and PAni/Cds nanocomposite.

### 3.2. FT-IR Spectroscopy

Fig.2.shows the FT-IR spectra of pure PANi, Pani/Cds nanocomposite and pure Cds. The presence of sharp peaks near  $1478$  and  $1559\text{ cm}^{-1}$  are attributed to C=C stretching of the benzenoid and quinoid rings, respectively. The peak at  $1240\text{ cm}^{-1}$  corresponds to C-N stretching of secondary amine in polymer main chain and can be clearly seen in both the sample. The

existence of absorption band at  $1144\text{ cm}^{-1}$  has been interpreted as originating from plane bending vibration of C-H, which was formed in the structure of B-N<sup>+</sup>-M, Q-N<sup>+</sup>-M and N=Q=N during protonation of CdS to polyaniline. Absorption band near  $2923\text{ cm}^{-1}$  is assigned to aliphatic C-H stretching of the polymer. A weak vibration absorption peak at  $414\text{ cm}^{-1}$  for Cd-S bond was observed, shows the concentrations of CdS in the composites was low.

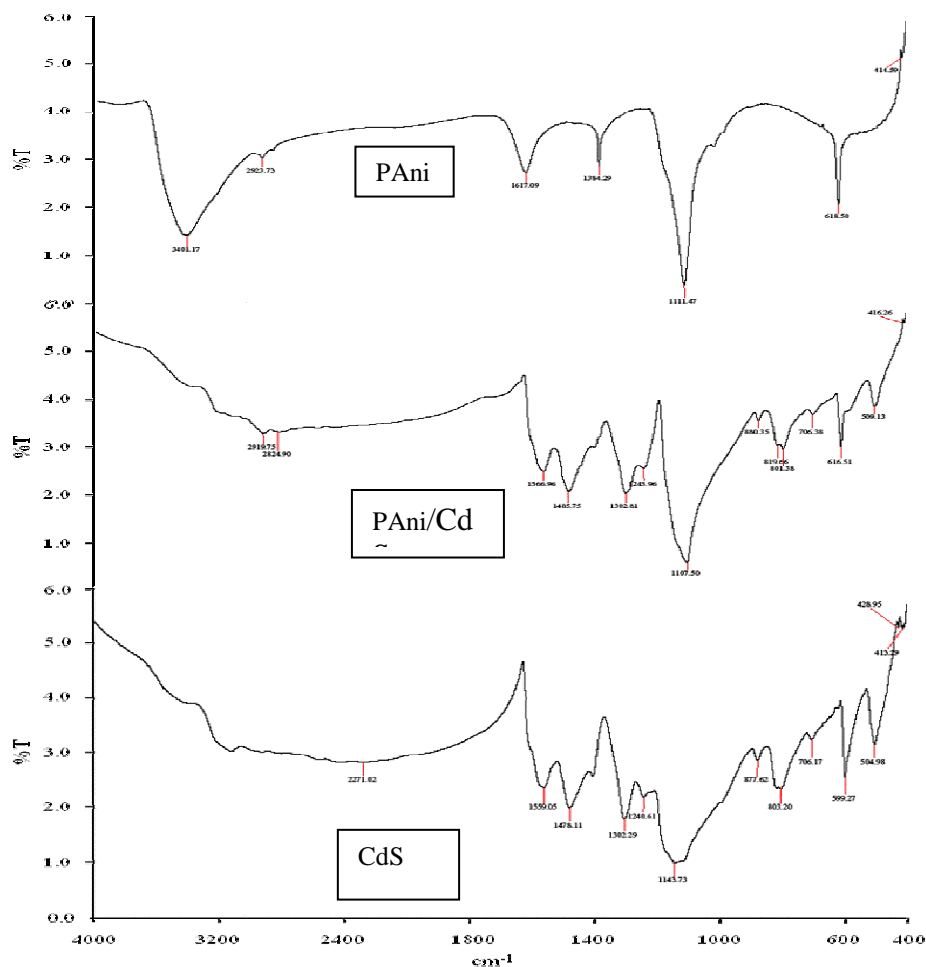
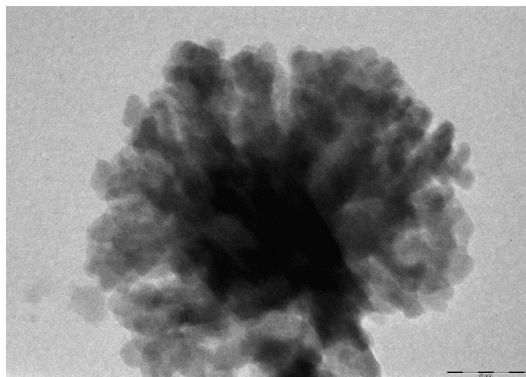


Fig.2 FT-IR spectra of Pure PANi, Pani/CdS nanocomposit, Pure CdS.

Fig 3. Shows the micrograph of CdS nanoparticles. The average diameter of nanoparticle is 21nm which was evenly distributed in the polymer matrix.

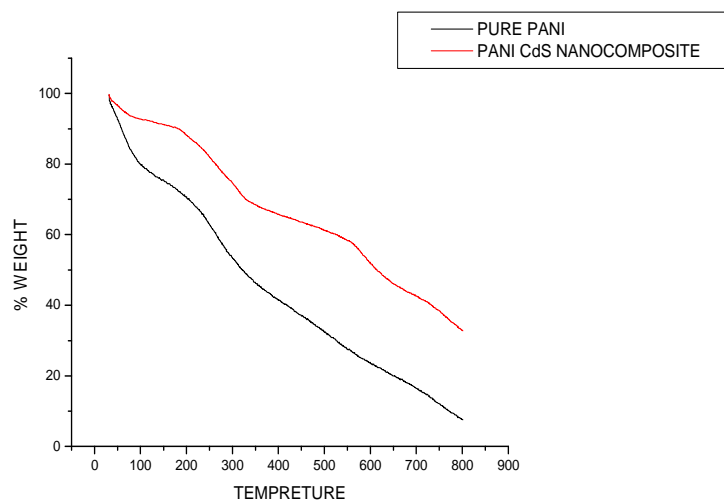


**Fig.3.TEM image of Pani/CdS nanocomposite.**

### 3.4. TGA Thermograph

The results of TGA analysis for pure PANI and PANI/CdS nanocomposites are

shown in Fig. 4. In the TGA thermograph of PANI/CdS, it can be observed that the losses of weight occurred around two temperature periods, ranging from 30 to 150 °C and around 400 to 600 °C. The first weight loss was mainly contributed by the elimination of impurities, residual water and unreacted monomers. The second step weight loss which is attributed to the degradation of polymer main chain. The 50% weight loss of Pure Pani is attributed at temperature 320°C and in case of Pani/Cds nanocomposite it is at 600°C. This clearly indicated that the thermal stability for the nanocomposites has been improved significantly as higher decomposition temperature as compared to pure PANI in the TGA profile. It might be related to the combination of CdS nanocrystalline in the polymer matrix, which yielded stronger binding force due to the interaction between CdS nanoparticles and the lone pair electrons of N atom in the polymer backbone<sup>12</sup>.



**Fig: 4.TGA of pure PANi and PANi/CdS nanocomposite**

### 3.5. Electrical Conductivity:

$$\sigma(T) = \sigma_0 \exp \left( -\frac{E_0}{2KT} \right)$$

The temperature dependence of the electrical conductivity data (in the middle range of temperature) fit the Arrhenius type of equation (1) in the temperature range investigated,

Conductivity than pure polyaniline reported in table 1. The activation energy  $\sigma_0$  (T) was calculated from Arrhenius equation presented in table 1.

Nanocomposite(wt % CdS)	Conductivity (S.cm <sup>-1</sup> )	Activation energy(eV)
5% Pani/Cds nanocomposite.	$1.437 \times 10^{-4}$	0.24033
10% Pani/Cds nanocomposite	$7.6201 \times 10^{-5}$	0.21233
15% Pani/Cds nanocomposite	$3.747 \times 10^{-4}$	0.2137
20% Pani/Cds nanocomposite	$9.5814 \times 10^{-5}$	0.12955
25% Pani/Cds nanocomposite	$1.744 \times 10^{-3}$	0.0694

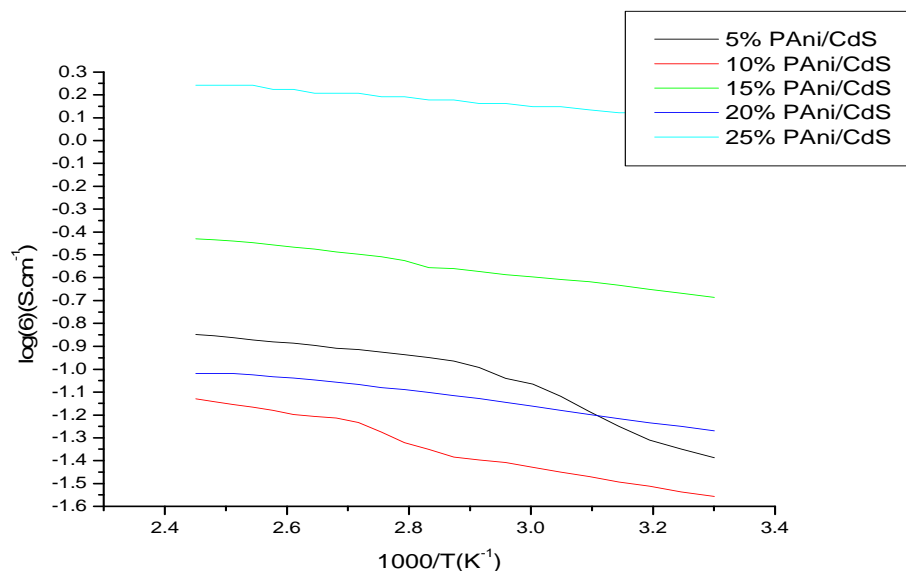


Fig.5. Electrical conductivity of PAni/Cds nanocomposite at different wt % of CdS.

The temperature dependence of electrical conductivity of CdS-polyaniline nanocomposite shown in figure 5. XRD and FT-IR spectra demonstrated that CdS nanoparticles had been successfully incorpo-

rated into polymer chain. From this result it is believed that intercalation of CdS nanoparticles in polyaniline were helped to increase the conductivity due to enhancement of crystallinity of CdS nanoparticles.

The conductivity of CdS-polyaniline (25%) ( $1.774 \times 10^{-3}$  S/cm) nanocomposite were greater than pure polyaniline ( $10^{-10}$  S/cm)<sup>13</sup>, and other PAni/CdS nanocomposite.

#### 4. CONCLUSIONS

Polyaniline-coated cadmium supplied nanocomposites have been synthesized via chemical oxidation technique. The XRD study revealed the increased in the degree of crystallinity of nanocomposit. The concentration of the CdS in nanocomposites was low as a very weak vibration absorption peak of Cd-S bonding at  $414 \text{ cm}^{-1}$  is observed in the FTIR spectrum. The average size of the nanocomposites is estimated to be 54 nm as observed in the TEM micrograph. The thermal stability for the nanocomposites has been improved as major mass losses occurred at higher decomposition temperature as compared to the pure polymer in the TGA profile.

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